PP-CBW/m-LLDPE/micro-CaCO₃ composite films manufactured from bumper waste by blown film extrusion

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Abstract. The synthesis of polypropylene-based car bumper waste (PP-CBW)/metallocene linear low-density polyethylene (m-LLDPE)/micro-CaCO₃ composite films for agriculture mulch films applications has been thoroughly investigated during this study. The chemical composition of these wastes was determined by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Three blends of various compositions were prepared using a twin-screw extruder, the pellets were then blown into films using a single screw extruder. The mechanical properties of the films were then studied and compared with the EN 13655, 2002 standards for agriculture mulch films applications. The results indicated that the use of an anhydride grafted polypropylene (MAH-g-PP) as compatibilizer improves the adherence at the interface between the polar acrylic paints present in the car bumper waste and the polymer matrix. Also, the presence of stearic acid surface treated micro-CaCO₃ improves considerably the mechanical properties of the composite when the amount of PP-CBW is less than 13 wt%. Using higher amount of PP-CBW improves the tear resistance properties in TD and MD but fails to increase the impact strength and the tensile properties in MD and TD.

1 Introduction

Polypropylene (PP) based materials account for more than 41% of the material in the automotive segments. When neat PP is modified by fillers ($CaCO_3$, alumina, silica, etc.) and mixed with ethylene-propylene rubber (EPR) or ethylene propylene-diene monomer (EPDM), thermoplastic olefin elastomers (TPOs) are formed. These polymers are currently the material of choice of car bumpers because of their excellent weatherability, elasticity, low density and relatively low cost. TPOs are multiphase materials presenting a nodular morphology, where the rubber phase is dispersed in the form of spherical particles in the PP matrix [1, 2]. Fillers are encapsulated by the rubber particles in a core-shell morphology or dispersed in the PP matrix depending on their size and surface treatment. TPOs are mostly used in car bumpers; the front bumpers are made of neat TPOs while the rear ones are often made from talc filled TPOs. TPOs recycling in the automotive industry is complex and challenging because of the oxidation of some bumper components, hence the deterioration of the mechanical properties, and the loss of the compatibility at the interphase [3]. Mechanical recycling is the most used method to recycle PP based materials, however, due to the sophisticated morphology of TPOs, the final properties of recycled products often do not meet car bumpers requirements [4, 5]. To reproduce original properties, TPOs are often mixed with a virgin polymer and with appropriate fillers and compatibilizers [6]. To improve the yield strength and Young's modulus of the recycled materials and to be able to use the recycled material in different applications, rigid fillers such as calcium carbonate ($CaCO_3$) are recommended [7]. To promote the adhesion between the rubber phase and the fillers, the surface of the rigid particles must be treated [7, 8]. On the other hand, to improve the adherence at the interface between the PP and a slightly polar rubber phase and consequently PP and rubber/filler interface a compatiblizer must be used [1].

Polyolefins and their reinforced blends are extensively used in packaging applications because of their low cost, low density, chemical inertness, good processability and good mechanical properties. As one of the most important micro-filler, $CaCO_3$ has been widely used in polyolefins as filler because of its low price, commercial availability and substantial improvement in mechanical properties stemming from its spherical shape morphology. Also, due to its high thermal conductivity, $CaCO_3$ shows high improvements in output and hence faster heating and cooling process cycles [9-12]. The surface of $CaCO_3$ particles is hydrophilic and polar and to improve their applicability as fillers and their adhesion with a non-polar matrix such as olefins, these particles are usually treated with stearic acid.

The purpose of this study is to recycle PP-based car bumper wastes to produce composite blown films for agriculture applications such as mulch films. The composite films were prepared by first blending, via a twin-screw extruder, a certain amount of the PP car bumper waste (PP-CBW) with a virgin metallocene based linear low-density

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polyethylene (m-LLDPE) matrix, using micro-$CaCO_3$ as filler and an anhydride grafted polypropylene (MAH-g-PP) as compatibilizer. Then, the composites pellets were blown into films on a single screw extruder. The mechanical properties of the composite films were then evaluated in order to choose the best blend for the mulch film application.

2 Experimental

2.1 Materials

PP-based car bumper wastes (PP-CBW) with specific density of 1.0 g/cc were supplied by a local Lebanese market. The chemical composition of these wastes was determined by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The three techniques reveal the presence of PP, PP-based elastomer, PE, $CaCO_3$, talc and acrylic paint in the waste. The car bumper wastes were first washed and then cut into small flakes using a milling machine. The flakes were then introduced into a twin-screw extruder with phenolic and phosphitic antioxidants and pelletilized. Phenolic antioxidant Irganox 1076 and phosphitic antioxidant Irgafos 168 were added at 0.1 wt% each in order to protect the composites against the damaging effects of thermo-oxidative degradation during and after processing. A vacuum suction system was utilized during twin screw extrusion in order to remove as much as possible the volatile polar paints from the bumper. Enable 2005, a metallocene catalyzed linear low-density ethylene-hexene copolymers (m-LLDPE1) with long chain branching were introduced with the car bumper wastes into the twin screw extruder to offer a high stiffness-toughness balance and a bubble stability. These polymers, having a density of 0.920 g/cc and an MFI of 0.5 g/10 min were purchased from Exxon Mobil. Exceed 1018, a metallocene catalyzed linear low-density ethylene-hexene copolymers (m-LLDPE2) were also used in one of the blends for their high tensile strength and toughness. These polymers having a density of 0.918 g/cc and an MFI of 1.0 g/10 min were also purchased from Exxon Mobil. MAH-g-PP was used as coupling agent to enhance the adhesion and dispersion of the polar paints coming from the PP-CBW in the polyolefin matrix. The MAH-g-PP used is an anhydride-modified PP random copolymer resin obtained from DuPont Packaging & Industrial Polymers. The ASCOM 60TM micro-$CaCO_3$, having a mean particle size of 1.8 μm, 7 μm top cut (D97), and a density of 2.7 g/cc, was obtained from Ascom Carbonate and Chemical Manufacturing Co. These particles are surface treated with stearic acid (1 wt%) to improve the compatibility with the nonpolar polyolefin matrix. Carbon black masterbatch was added to the blown film blends at 3 wt% loading in order to provide blackish color, high opacity and good weathering performance to the produced films.

2.2 Manufacturing Process

The purpose of this work is to recycle PP-based car bumper wastes to produce nanocomposite films. A Qingdao intermeshing co-rotating twin-screw extruder (L/D ratio of 48 and a screw diameter of 22 mm) with pelletizing unit was utilized for this study. The twin-screw extruder is equipped with a modular screw profile. The screw is composed of right-handed elements, left handed elements and kneading blocks, with 6 separate shear mixing zones. The temperature profile from the feeding zone to the die was set as follows: 170-200-205-210-215-220-220°C. A vacuum suction system was always utilized during twin screw extrusion to remove as much as possible the volatile polar paints coming from the car bumper waste, which can cause gels and deterioration of key mechanical properties. Table 1 shows the composition of the different blends.

Table 1. Composition of the different blends

Blend name	Blend A	Blend B	Blend C
mLLDPE1 (wt%)	35.8	57.8	53.8
mLLDPE2 (wt%)	15	0	0
PP-CBW (wt%)	20	13	20
Micro-$CaCO_3$ (wt%)	28	28	25
MAH-g-PP (wt%)	1	1	1
Irgafos 168 (wt%)	0.1	0.1	0.1
Irganox 1076 (wt%)	0.1	0.1	0.1

The resulting composite pellets were subsequently processed at 100% loading in a KR Horsens Formac Polifilm monolayer blown-film extruder with a die diameter of 8 cm, to produce micro-composite films. The film is pulled in the transverse direction (TD) to reach the ultimate diameter of the bubble. At the same time, it is being pulled in the machine direction (MD) by the nip rollers movement. By pulling the film into the MD and TD directions, the molecules become orientated in both directions, resulting in tougher films with balanced tensile, tear and shrink properties. In this

work, the blown film trials were carried out at a blow-up ratio (BUR) equal to 2.0, which is the ratio of diameter of the bubble to the diameter of the extrusion die. The temperature profile used for the screw from the feeding zone to the die was as follows: 200-210-220-230-230°C. The produced films have an average thickness equal to 50 µm.

2.3 Characterization method

The chemical composition of PP car bumper wastes was studied by FTIR using a Bruker Tensor II FTIR Spectrometer operating in attenuated total reflectance (ATR) mode according to ASTM E1252. ATR measures surface properties of the sample with a penetration depth of 0.5 to 2 µm into the sample. 32 scans at a resolution of 4 cm^{-1} were used.

The melting behaviour of the PP-CBW was investigated by differential scanning calorimetry (DSC) using a Netzsch DSC Polyma 214 and according to ASTM D3418 standard. For each sample, a mass of 10 mg was heated under a nitrogen atmosphere (20 mL/min) over a temperature range between 25 ºC and 200 ºC using a DSC cycle of heating-cooling-heating. The first heating is performed to erase all the thermo-mechanical history. During the cooling phase, the exothermic crystallization peak is identified, the endothermic melting peak occurs during the heating phase. The heating and cooling rates were set at 10°C/min. The cooling and second heating thermograms were recorded to study the composition and the crystallization kinetics. The degree of crystallinity X_c was estimated by the following equation:

$$X_c\ (\%) = (\Delta H_m)/(\Delta H_m^0) \times 100 \tag{1}$$

Where X_c is the crystallinity, ΔH_m the melting enthalpy in J/g, ΔH_m^0 is the theoretical melting enthalpy of perfectly crystalline polymer. The reference heat of melting of pure polymers was taken from the literature and corresponds to 207.1 J/g for pure PP.

Tensile testing of plastic films was performed on a LLOYD universal testing machine in accordance with ASTM D882–12. The tests were performed at ambient temperature, using a 1 kN load cell with a crosshead speed of 500 mm/min at which the sample breaks freely. A minimum of 5 test specimens were tested from each batch where the average data will be presented later in this paper.

The Elmendorf tear tests were carried out according to ASTM D1922. Before initiating the test, the plastic films are cut in rectangular shape in two directions (MD and TD), in a way to fit the machine clamps of the Elmendorf tear resistance tester. The sample is clamped, and the pendulum impact tester is fixed in the raised position. A cutting knife in the tester is used to create a slit in the sample and the pendulum is released to propagate the slit. The energy loss by the pendulum is used to calculate an average tearing force.

Thermogravimetric analysis (TGA) was performed using a Netzsch TG209 F3 Tarsus thermogravimetric analyzer. Samples weighing about 10 mg each were heated up to 900°C in nitrogen at a rate of 10°C/min. The onset decomposition temperatures ($T_{d,onset}$), as well as the first derivative peak temperature (T_{peak}), of the PP-CBW were analyzed in order to judge the decomposition behavior of the material. In addition, the organic and inorganic components were identified and quantified by the thermal decomposition behavior.

The dart drop impact test was performed according to ASTM D1709. This test implies dropping a dart at a single drop height on a film while varying the weight of the dart; if the test fails (rupture of the film), a missile weight is removed, and otherwise the same missile weight is added. Depending on the expected toughness of the test sample, either Method A or Method B is chosen. Method A that specifies a dart with a 38.1 mm diameter dropped from 0.66 m was adopted in this work. The dart weight and the test results ("X" for failure/ "0" for no failure) are recorded. A minimum of 20 trials and 10 X's are required to proceed to the results treatment step. If N > 10, additional specimens are tested until the number of 0's reaches 10. The dart impact failing weight *WF* was calculated using equation:

$$WF = W_0 + \Delta W(A/N - 0.5) \tag{2}$$

Where W_o: smallest weight at which the film has ruptured;
ΔW: differential weight added and subtracted;
A: Σ i*n; i: integer (i=0 for W_o going up to the heaviest weight);
n: number of failures for a certain weight;
N: total number of X's (usually equal to 10); if N>10 we omit some of the "X" results.
Therefore, the dart impact strength (in g/mic) is equal to *WF* divided by the average thickness of the film.

3 Results and discussion

3.1 PP-CBW COMPOSITION

The FTIR spectrum of the car bumper wastes is shown in Figure 1. The IR spectrum reveals the presence of PP, PP-based elastomer, PE and acrylic paint. Peaks at 1719 cm^{-1} and 1776 cm^{-1} are associated with the acrylic paint, while the

absorbance peak at 1544 cm^{-1} is associated with PP-based elastomer. The peak at 726 cm^{-1} corresponds to PE fraction coming from both the Vistamaxx and the PP block copolymer. The characteristic pics of PP are at 2950, 2915 and 2838 cm^{-1} corresponding to the C-H stretching; at 1455 cm^{-1} attributed to CH_2 bending; at 1377 attributed to CH_3 bending; at 1166 cm^{-1} corresponding to C-H bending; at 840 cm^{-1} attributed to CH_2 rocking vibration and C-CH_3 stretching. The peak at 808 cm^{-1} concerns CH_2 rocking head-tail structure of PP which is characteristic structure of PP crystals [13]. The peaks at 1014 cm^{-1} and at 457 cm^{-1} confirm the presence of talc in the bumper.
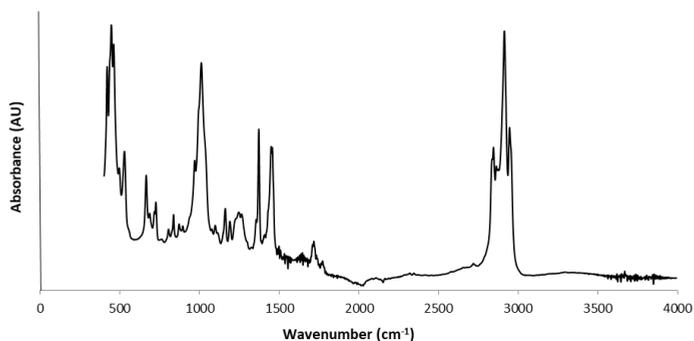

Fig. 1. FTIR-ATR spectrum of the PP-CBW.

The DSC thermogram (Figure 2) confirms the presence of a high-density PE (melting point (T_m) = 126°C and melt crystallization temperature (T_c) = 116°C), along with a nucleated PP block copolymer resin (T_m = 164°C and T_c = 125°C). From the calculation, the degree of crystallinity of the whole car bumper was determined to be equal to 45%.
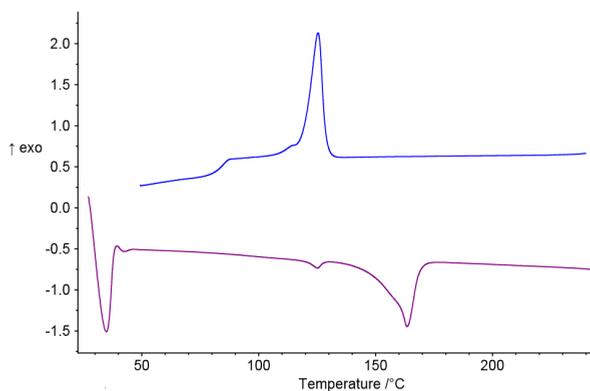

Fig. 2. DSC thermogram of PP-CBW.

The extrapolated onset temperature ($T_{d,onset}$), the first derivative peak temperature (T_{peak}) where the maximum rate of decomposition occurs, as well as the residual mass in the bumper waste were determined by the TGA and DTG (derivative plot of TGA) as shown in Figure 3. The residual mass corresponds to the inorganic content of the sample. From these values we can estimate the amount of organic phase. TGA analysis shows the standard PP $T_{d,onset}$ at 443°C and T_{peak} at 468°C. The analysis shows also that the amount of the PP organic phase is equal to 84%, the amount of $CaCO_3$ is equal to 5% and the amount of inorganic talc residue is equal to 9%.
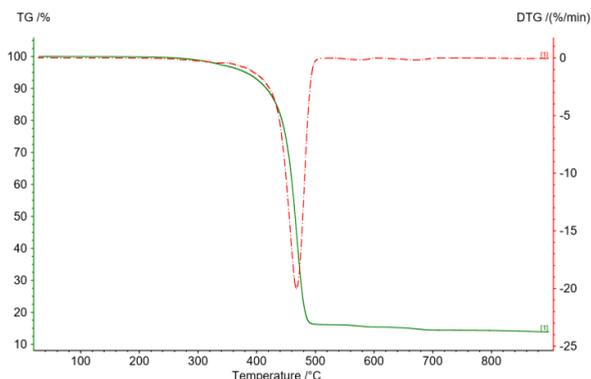
Fig. 3. Thermal decomposition behaviour of PP-CBW.

3.1 MECHANICAL PROPERTIES

The mechanical results of the three composites films prepared are summarized in Table 2. Table 2 reveals that good mechanical properties were obtained when a content of 13 wt% of PP-CBW and a load of 28% micro-CaCO$_3$ (Blend B) were used. This result indicates a good dispersion, a good miscibility and a good interfacial adhesion between the various components of the blend.

Table 2. Mechanical properties of the blends A, B and C.

Blend name	Blend A	Blend B	Blend C
Dart impact g/mic (Method A)	1.07	5.58	0.75
Tear resistance (g/mic) MD	12.94	10.51	6.80
Tear resistance (g/mic) TD	28.16	26.63	14.80
Tensile strength at break MD (MPa)	15.43	19.02	10.40
Tensile strength at break TD (MPa)	10.75	19.48	8.70
Elongation MD at break	196	243	403
Elongation TD at break	-	298	472

The use of MAH-g-PP as compatibilizer considerably improves the adherence at the interface between the polar acrylic paints and the polymer matrix. Also treating micro-CaCO$_3$ with stearic acid improves the dispersion of the particles in the non-polar polymer. As expected, increasing the amount of PP-CBW to 20% in Blend A and Blend B decreases significantly the dart drop impact strength and the tensile strengths in TD and MD direction. This could be due to a loss of compatibility and adhesion between the various phases, as higher amount of coupling agent is needed with the higher amount of polar paint. This result shows that mechanical recycling of TPOs couldn't reproduce the original sophisticated morphology of TPOs when a waste load higher than 13% is used in the composite material. The loss of compatibility is illustrated by the reduction of the tensile and impact performance when the amount of PP-CBW increases in the blend. Moreover, the loss of impact properties is further linked with the higher stiffness/embrittlement effect of the PP-CBW as opposed to the tougher m-LLDPE resins. Comparing properties of Blend B and Blend C, an increase in the amount of micro-CaCO$_3$, from 25 wt % loading to 28 wt % loading, along with a decrease in the PP-CBW content, from 20 wt. % to 13 wt. %, resulted in a drastic improvement in MD and TD tear resistance and dart drop impact strength values. Tear resistance improvement is linked to more obstacles to tear propagation with higher loading of calcium carbonate, and the improvement of dart drop impact strength can be linked to enhanced material compatibilization with higher MAH-g-PP to paint ratio. Also, the spherical morphology of the micro-CaCO$_3$ particles improves the impact strength of the polymer in all directions (balanced properties) by filling the voids and by forming a continuous network transferring or dissipating the energy. Interestingly, for the same wt % of CaCO$_3$ (Blend A vs. Blend B) increasing the load of recycled polymers improves the tear resistance properties, due to presence of PP-based elastomer (such as Vistamaxx resin) in the PP-CBW. Furthermore, a significantly higher MD tear resistance in Blend A is observed due to the incorporation of m-LLDPE2 (15 wt %). Thus, the MD tear resistance of mLLDPE2 is significantly higher than that of m-LLDPE1 resin (9.8 g/mic vs. 3.5 g/mic).

4 Conclusion

m-LLDPE/PP-CBW/micro-CaCO$_3$ composite blown films have been successfully produced and characterized in this study. These films can be used as mulch films for agriculture applications since the obtained properties comply with the EN 13655, 2002 standards. The composition and the amount of organic and inorganic phases of PP-CBW was revealed by FTIR, DSC and TGA. The FTIR showed that the car bumper waste is a mixture of PE, PP with the presence of talc, acrylic paints, PP-based elastomers. The TGA analysis showed that the amount of the organic phase is equal to 84% and that the inorganic phase consists of a mixture of 5% wt CaCO$_3$ and 9% wt inorganic talc residue. We investigated thoroughly during this study the effects of two different percentages of PP-CBW on the mechanical properties of the composites. The good mechanical results obtained for 13 wt% PP-CBW showed that the recycled PP-CBW waste could be used with the micro-CaCO$_3$ as filler and m-LLDPE as a polymer matrix. The improvement of the tensile strength and impact properties with decreasing the amount of PP-CBW revealed that the use of MAH-g-PP as a coupling agent is necessary to improve the compatibility of the paints with the polymer matrix. The micro-composite exhibited a drastic improvement in MD and TD tear resistance and dart drop impact strength values when the amount of CaCO$_3$ increased, along with a decrease in the PP-CBW content. For the same amount of micro-CaCO$_3$, increasing the load of recycled polymers in addition to loading of m-LLDPE2 improved the tear resistance properties, especially in the MD. Several recommendations for future work could be suggested to reduce the amount of virgin matrix in the composite, such as increasing the amount of coupling agent and varying the ratio of m-LLDPE1/m-LLDPE2 during compounding.

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